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MILTON WHITNEY, Chief.

U. S. DEPARTMENT OF AGRICULTURE,

BUREAU OF SOILS,

Washington, D. C., May 28, 1912.

SIR: I have the honor to transmit herewith the manuscript of an article on the Extraction of Potash from Silicate Rocks, by William H. Ross, Scientist in Physical and Chemical Laboratory Investigations, Bureau of Soils, and to request that it be published as Circular No. 71, of this bureau.

Very respectfully,

MILTON WHITNEY,

*Chief of Bureau.*

Hon. JAMES WILSON,

*Secretary of Agriculture.*

## THE EXTRACTION OF POTASH FROM SILICATE ROCKS.

The potash-bearing minerals of the United States may conveniently be divided into three classes, as follows: (1) Alunite and similar minerals; (2) the greensand marls; and (3) the igneous rocks.

Alunite is a hydrated sulphate of aluminum and potassium. It differs from the minerals of the other two groups in that the potassium is readily available by simple ignition of the mineral to a dull red heat.<sup>1</sup> When occurring in sufficient quantity and purity alunite is thus a possible economic source of potash and has long served as a source of potassium alum in Italy and other countries. Its occurrence in this country is limited to comparatively small deposits in Utah, Colorado, and Nevada, the largest so far known, near Marysville, Utah, having been recently described.<sup>2</sup>

Greensand, or glauconite, is essentially a hydrated silicate of iron and potassium, but it is extremely variable in composition and never occurs pure. It is formed through the interaction of various alteration products, and organic matter is believed to play a part in its formation,<sup>3</sup> which would explain its occurrence in the marl deposits

<sup>1</sup> Waggaman, Circular No. 70, Bureau of Soils, U. S. Dept. Agr.

<sup>2</sup> Butler and Gale, Bul. U. S. Geol. Survey, No. 511.

<sup>3</sup> Clarke, Bul. U. S. Geol. Survey, No. 491, p. 942.

of Kentucky, New Jersey, Tennessee, and other States. Like the minerals of the third group it is a refractory silicate, and the potash which it contains is not readily available.

The potash-bearing silicates are among the most widely distributed minerals and occur as constituents of nearly all rocks. The principal minerals of this class from the point of view of the potash which they contain are orthoclase, or microcline, muscovite, and leucite. Millions of tons of rock containing one or more of these and related minerals with a potash content in the neighborhood of 10 per cent are to be found widely distributed all over the globe. It is for this reason that the igneous minerals, particularly the potash feldspars, are most often spoken of as a source of potash salts.

In Table I is given sample analyses of the most important potash-bearing minerals:

TABLE I.—*Analyses of potash-bearing minerals.*

	(1)	(2)	(3)	(4)	(5)
SiO <sub>2</sub> .....	0.22	51.56	65.87	44.39	50.23
TiO <sub>2</sub> .....					2.27
Al <sub>2</sub> O <sub>3</sub> .....	37.18	6.62	19.10	35.70	11.22
Fe <sub>2</sub> O <sub>3</sub> .....	Trace.	15.16	.....	1.09	3.34
FeO.....		8.33	.....	1.07	1.84
MgO.....		.95	None.	.....	7.09
CaO.....		.62	.20	.10	5.99
Na <sub>2</sub> O.....	.33	1.84	2.56	2.41	1.37
K <sub>2</sub> O.....	10.46	4.15	12.24	9.77	9.81
H <sub>2</sub> O.....	12.99	10.32	.64	5.88	2.65
P <sub>2</sub> O <sub>5</sub> .....	.58	.....	.....	.....	1.89
SO <sub>3</sub> .....	38.34	.....	.....	.....	.74
Fl.....				.42	.50
Other constituents.....					1.68
	100.10	99.55	100.61	100.83	100.62

(1) Alunite from Marysville, Utah. Selected specimen. Analysis by W. T. Schaller, Bul. U. S. Geol. Survey, No. 511, p. 8.

(2) Glauconite from greenshell marl. Hanover Co., Virginia. Analysis by M. B. Corse and C. Baskerville, Am. Chem. Jour., 14, 627.

(3) Ground commercial feldspar from quarry of J. B. Richardson & Sons, Bedford, Ont. Analysis by George Steiger, Bul. U. S. Geol. Survey, No. 420, p. 9.

(4) Muscovite from Auburn, Maine. Analysis by R. B. Riggs, Bul. U. S. Geol. Survey, No. 419, p. 286.

(5) Leucite-bearing rock, Wyoming. Analysis by W. F. Hillebrand, Bul. U. S. Geol. Survey, No. 512, p. 11.

The desirability of finding some economical way of extracting potash from these minerals has long attracted the attention of various investigators, and numerous patents have been issued covering processes which are claimed to solve this difficult problem.

The increasing yearly demand for potash salts in connection with artificial fertilizers has of late renewed interest in this direction, and in some cases companies have been organized for the purpose of manufacturing potash by one or other of the various processes which have been proposed, but up to the present no potash prepared in this way has been placed on the market.

Practically all methods yet proposed, in principle at least, have been covered by patents. A comparative study was therefore undertaken

of all the processes for which patents have been allowed, with a view to finding what methods, if any, give promise of being practicable commercially. It is thought advisable to publish some of the results thus far obtained.

The most convenient way of determining the alkalies in silicate rocks is the well-known J. Lawrence Smith method. According to the directions usually given for this method, 0.5 gram of the ground material is mixed with an equal weight of pure ammonium chloride and 4 grams of calcium carbonate. On igniting the mixture gently at first, the ammonium chloride is volatilized and part of the calcium carbonate is converted into calcium chloride. These two compounds of calcium when heated at a temperature of about 1,000° C. with feldspar, or other silicate rock, bring about its decomposition, and any potash present is converted quantitatively into potassium chloride. The same result is obtained if the proper amount of calcium chloride is used instead of ammonium chloride in the first place.

Of the many patents which have been issued for extracting potash from silicate rocks, at least four may be considered modifications of the J. Lawrence Smith method, since the essential feature of each consists in heating the potash-bearing material with calcium carbonate and some metallic chloride.

The first of these, United States patent No. 513001, was issued to H. S. Blackmore in 1894. To produce a soluble potassium salt according to this patent, orthoclase, reduced to a fine powder, is mixed with finely powdered calcium chloride in about equal proportions to the potassium silicate present. To the mixture is then added an excess of calcium oxide and a sufficient quantity of water to render the entire mass moist. This is introduced into a sealed furnace, or retort, and heated to a temperature of about 1,100° C., whereby the water mixed with the mass is converted into superheated steam at a high pressure, which is supposed to assist materially in the transformation of the orthoclase into soluble potassium chloride and insoluble silicates of calcium and aluminum. The heating is continued for about two hours, and, after cooling, the mass is placed in vats and lixiviated.

The part of the process as patented which requires the moist mass to be heated in a sealed furnace to a temperature of 1,100° C. could obviously not be carried out on a large scale, for it would not be feasible to make a furnace which would stand the pressure produced at this temperature.

In 1900 United States patent No. 641406 was granted to G. J. Rhodin for obtaining soluble potassium salts from feldspar. In carrying out the process according to this invention, 1 part of feldspar is mixed with 1 part of lime and 0.2 part of sodium chloride,

all in a finely powdered condition. The mixture is then heated in a closed vessel of iron or other material, or else in an open-hearth or blast furnace, to a bright yellow heat and maintained at that temperature for a considerable time, care being taken not to melt or fuse the mixture. The cooled mass which still remains in a powder may be applied directly as a manure, since the potash present is claimed to be rendered available by the treatment, or it may be separated from the mass by treatment with acids.

In 1907 United States patent No. 869011 was issued to Ralph H. McKee for a process for producing potassium compounds from potash-bearing material containing mica by essentially the same treatment as that covered by Rhodin's patent for the extraction of potash from feldspar.

United States patent No. 987436 was granted to A. S. Cushman in 1911 for a method for obtaining potash from silicate rocks. According to this method the feldspathic rock is reduced to as fine a subdivision as possible and mixed with finely powdered quicklime in the proportion of 100 parts of the rock to 20 parts of lime. The mixture is then spread on a suitable conveyor, as belt or drum, in the form of a bed having a thickness from three-eighths to one-half inch. To the surface of this bed is now applied a solution of calcium chloride in separate drops, and of such a concentration that the amount of calcium chloride added should be sufficient to supply chlorine in quantities at least molecularly equivalent to the total alkali contained in that portion of the feldspar which becomes aggregated into lumps on the addition of the solution. The aggregates, which harden quickly at ordinary temperatures, are separated from the unconverted powder by screening, and are then heated in a rotary kiln at a temperature preferably, but not necessarily, below the point at which a substantial part of the potassium chloride is sublimed. The product is discharged continuously from the furnace in lumps and may be crushed for use directly as a fertilizer; or the potassium chloride may be extracted by means of water and recovered from the solution, or utilized therein in any preferred way.

From a comparative study which was made of these patents it does not appear that the use of sodium chloride has any advantage over calcium chloride. The latter is a by-product obtained in large quantities in the manufacture of sodium carbonate, and is somewhat more effective than the former in bringing about complete decomposition of the feldspar, but when limited amounts of the reagents are used more potash is rendered soluble with the use of sodium chloride than with calcium chloride. In Table II are given the percentages of the total potash in the feldspar which have

been rendered soluble on heating a given amount of feldspar at 1,000°–1,050° C. with varying amounts of calcium carbonate and calcium chloride, and with calcium carbonate and sodium chloride. The feldspar used in these experiments was ground to pass a 100-mesh sieve and contained 13.72 per cent of  $K_2O$ , and 2.18 per cent of  $Na_2O$ .

Table II.—*Showing percentages of alkalies rendered soluble when feldspar is ignited with varying amounts of calcium carbonate and calcium chloride, and with calcium carbonate and sodium chloride.*

Feldspar.	CaCO <sub>3</sub> .	CaCl <sub>2</sub> .	NaCl.	Time of ignition.	Na <sub>2</sub> O obtained in percentage of feldspar.	K <sub>2</sub> O obtained in percentage of feldspar.	Percentage of K <sub>2</sub> O in feldspar rendered soluble.
Gram.	Grams.	Gram.	Gram.	Hours.			
1	1	0.25	.....	2	1.8	8.2	59.8
1	1	.50	.....	2	1.6	9.4	68.5
1	2	.25	.....	2	1.8	10.7	78.0
1	2	.50	.....	2	2.0	13.0	94.8
1	3	.25	.....	1	1.8	10.8	78.7
1	3	.25	.....	2	1.8	10.9	79.4
1	3	.50	.....	1	2.0	13.0	94.8
1	3	.50	.....	2	2.0	13.2	96.2
1	3	1.00	.....	2	2.2	13.6	99.1
1	1	0.25	.....	2	.....	9.4	68.5
1	1	.....	.50	2	.....	11.2	81.6
1	2	.....	.50	2	.....	11.7	85.3
1	3	.....	.25	2	.....	9.4	68.5

In these experiments the results show that while a considerable portion of the potash was rendered available when using approximately the proportions of the reagents stated in the patents, the total potash in the feldspar was not rendered soluble in this way at the temperature specified. Thus, when 1 part of feldspar is ignited with 1 part of calcium carbonate and 0.25 part of calcium chloride, which is 0.05 part in excess of that equivalent to the alkalies in the feldspar, only about 60 per cent of the potash in the feldspar is rendered soluble. Increasing the proportions of calcium carbonate and calcium chloride used produces a comparatively small increase in the amount of soluble potash obtained, and complete decomposition of the feldspar only takes place when one part is ignited, under the conditions of the experiment, with about 1 part of calcium chloride and about 2 to 3 parts of lime. When this proportion of the reagents is used, considerable variation in the temperature of ignition will give the same results, and almost the entire amount of the potash is rendered soluble at a temperature below the melting point of potassium chloride.

The results obtained on igniting feldspar with lime and sodium chloride are in agreement with those published by Rhodin,<sup>1</sup> the

<sup>1</sup> J. Soc. Chem. Ind., 20, 439 (1901).

author of the patent covering this process, who only claimed an extraction of about 41 per cent of the potash in the feldspar when using the proportion of the reagents stated in the patent, viz, 1 part feldspar, 1 part lime equal to 1.8 parts calcium carbonate, and 0.2 part sodium chloride. It was pointed out, however, that a more favorable result was obtained by using a larger amount of salt with a smaller amount of lime. Thus, when 100 parts of feldspar were ignited to 900° C., with 40 parts of lime and 40 parts of salt, about 70 per cent of the potash in the feldspar became soluble, which agrees with the value given in the table for approximately this proportion of the reagents.

Unless a large excess of calcium chloride is used, when ignited with feldspar and lime, no vitrification takes place on heating to a temperature up to 1,050° C. The ignited mass remains in the form of a powder, and consequently the soluble material present can be readily leached out without the necessity of any previous grinding of the mass. The same statements hold true when sodium chloride is used, but with a more limited variation in the proportions of the reagents which may be taken. Thus, a hardened mass is obtained when 1 part of feldspar is ignited to 1,050° C., with 1 part of calcium carbonate and 0.25 part of sodium chloride, but if the proportion of calcium carbonate is doubled the mass remains in a powdered form. When calcium chloride is used, the mass does not harden on ignition, even with 1 part of calcium carbonate.

On account of its simplicity, the method of decomposing feldspar by heating with calcium carbonate and with calcium chloride (or sodium chloride) could undoubtedly be carried out on a large scale without involving any serious mechanical difficulty, and the method would thus be a practical one providing the value of the products obtained would compensate for the expense involved. Although pure feldspar may be obtained which contains upward of 15 per cent potash, the average grade of feldspar which could be mined on a large scale would undoubtedly contain less than 10 per cent. If potash be quoted at 66 cents a unit,<sup>1</sup> then the potash in a ton of feldspar containing even 10 per cent of this constituent would be worth only \$6.60 when converted into a soluble form. It is thus evident that the value of the potash alone will not compensate for its extraction by this process, or by any modifications of it for which patents have been granted; nor is it at all likely in view of the comparatively low percentage of potash in all silicate rocks that any process can be devised which will prove so simple that the value of the potash alone will pay for its extraction. It seems safe to say, therefore, that any method to be economical must produce at the same time other products of value in addition to the potassium.

<sup>1</sup> Estimated from prices quoted by the German Kali Works.

One of the first patents on a process for converting the insoluble potash in feldspar into a soluble form was issued in 1856 to Charles Bickell (United States patent No. 16111). The process consists in heating in a reverberatory, or other suitable furnace, to a light-red heat for about 2 hours, 1 part feldspar, 0.5 part phosphate of lime, and 3 or 4 parts of lime, all in a finely divided state. According to the patent the potash becomes available by this treatment, and may be extracted in a caustic state by lixiviating with water, or the mass may be used directly as a manure.

At first sight this process seemed particularly attractive, for if both the potash and phosphoric acid were rendered available by this treatment, as claimed by the patent, the method might be an economical one, since when used as a fertilizer no separation of the constituents would be necessary, and the mixture would be of value for its phosphoric acid as well as its potash content.

It was found, however, that the calcium phosphate has a passive effect in this treatment of the feldspar, and that no greater decomposition was produced in this way than when it was heated with calcium carbonate alone.

Thus when 1 gram of feldspar, 0.5 gram of calcium phosphate, and 3 grams of calcium carbonate were mixed and ignited for two hours at 1,000° C. in a J. Lawrence Smith crucible, the amount of potash rendered soluble only amounted to about 2 per cent of the feldspar. The amount of soluble potash obtained when 1 gram of feldspar and 3 grams of calcium carbonate were ignited in the same way likewise amounted to approximately 2 per cent, but in each case the greater part of the residue remaining after extracting with water was decomposed when treated with dilute hydrochloric acid, the potash going into solution.

When the temperature was increased to about 1,200° C. the soluble potash amounted to 5 per cent of the feldspar, and the extracted residue was then found to be readily and completely decomposed by hydrochloric acid. From this solution was obtained the remaining portion of the potash which did not dissolve on digesting with water.

The crucible in which these ignitions were made was closed with a cap, and as this end of the crucible was not ignited, there was little tendency for the potash to escape, but when the ignition was made in an open platinum dish in a furnace at a temperature of about 1,400° C. the potash in the feldspar was found to have been completely lost by volatilization.

In carrying out this experiment the feldspar was first dried to constant weight by heating in a muffle furnace at 1,000° C. The calcium oxide used was likewise reduced to constant weight by igniting chemically pure calcium carbonate at a temperature of 1,400° C.

for several hours. One gram of the feldspar and 1.68 grams of calcium oxide, equivalent to 3 grams of calcium carbonate, were then well mixed and ignited in an open dish in the furnace at 1,400° C. for one hour. The weight of the mixture was found to have decreased by 0.1606 gram, which is equal to 16 per cent of the feldspar. The residue was then analyzed for potassium, but only a trace was found.

The experiment was then repeated, using ten times the amount of feldspar and a corresponding amount of calcium oxide. The same care was taken as before to reduce each constituent to constant weight before mixing. After igniting for one-half hour the loss in weight of the mixture amounted to 1.3912 grams, equal to 13.9 per cent of the feldspar. On repeating the ignition for one hour a further loss in weight of 0.1630 gram took place, which was increased to 0.1768 gram on igniting for one hour longer, making a total loss of 1.5680 grams, equal to 15.7 per cent of the feldspar. Since the feldspar was shown by analysis to contain 15.9 per cent of  $K_2O + Na_2O$ , it would thus appear that the greater part of the alkalies in the feldspar were driven off in the form of oxides. This was confirmed by an analysis of the residue, which contained less than 0.2 per cent of total alkalies.

The hardened mass remaining after ignition strongly resembled cement clinker, and that the product obtained by igniting feldspar and lime together contains all the essential elements of a cement is well known. Using the feldspar and lime in the proportions of 1 to 1.68, a clinker approaching the composition of Portland cement is obtained.

Thus, if 1 part of feldspar assumed to contain the theoretical amounts of potash, alumina, and silica loses the first-named constituent, amounting to 0.17 part when ignited with 1.68 parts of calcium oxide, or 3 parts of calcium carbonate, then the clinker which remains will equal 2.51 parts, and will have the percentage composition given in Table III. In the second and third columns are also given the minimum and maximum limits of the constituents of good Portland cement.<sup>1</sup>

TABLE III.—*Comparison of the composition of feldspar-lime clinker with that of Portland cement.*

Constituents.	Feldspar-lime clinker.	Portland cement.	
		Minimum.	Maximum.
Silica.....	25.8	19	26
Alumina.....	7.3	4	11
Lime.....	66.9	58	67
Ferric oxide.....	0	2	5
Magnesia.....	0	0	5
Sulphuric acid.....	0	0	2.5
Alkalies.....	0	0	3

<sup>1</sup> Bleininger, Bul. Ohio Geol. Survey, No. 3, p. 197.

This shows that all the constituents of pure feldspar-lime clinker lie between the limits allowable in a good Portland cement, and that ferric oxide is the only necessary constituent absent. If commercial feldspar and lime were used, however, this would no doubt also be supplied in sufficient quantity, and at the same time the silica and lime would be reduced more closely to the mean of that found in a good Portland cement, providing the feldspar does not contain an excessive amount of free silica.

In order that a clay may be suited for the manufacture of cement it should have a percentage ratio of silica to alumina of from 3 to 1 to 4 to 1.<sup>1</sup> The ratio of these two constituents in feldspar is 3.5 to 1. In muscovite and leucite of theoretical composition the proportion of silica to alumina is less than 3 to 1, but in commercial samples of leucite-bearing rocks the ratio is usually greater than 4 to 1.

A clinker of the same ultimate composition as that which results when feldspar and lime are heated together may also be obtained when part of the lime is replaced by sufficient calcium chloride to be equivalent to the potash and soda in the feldspar, the total calcium used remaining the same as before. In carrying out this experiment the feldspar and lime were ignited to constant weight as already described, and the calcium chloride thoroughly dried by heating in an air bath below its melting point. Ten grams of the feldspar were well mixed with 2.0050 grams of calcium chloride and 15.7895 grams of calcium oxide, and the mixture then ignited in an open dish in the furnace at 1400° C. By this treatment the alkalies are volatilized as the chlorides.<sup>2</sup> On igniting for one-half hour the weight lost by the ignited mass amounted to 2.5632 grams, equal to 25.63 per cent of the feldspar. When expressed as the chlorides the percentage of alkalies in the feldspar used amounted to 25.82 per cent. It would appear, therefore, that practically the whole of the alkalies in the feldspar were volatilized during the first half hour of ignition. On continuing the ignition for one hour longer the additional decrease in weight which took place amounted to only 0.0090 gram. The residue was then analyzed for potassium and chlorine, but only a trace of each was found.

This shows that the volatilization of the potash in feldspar takes place more rapidly when part of the lime is replaced by calcium chloride than when the feldspar is ignited with lime alone, but in each case the ultimate composition of the residue obtained is the same. Any excess of calcium chloride used above that equivalent to the potassium in the feldspar is slowly decomposed at the temperature at which the ignitions were made, leaving behind the oxide of calcium.

<sup>1</sup> Bleininger, loc. cit., p. 223.

<sup>2</sup> Herstein, J. Ind. Eng. Chem. 3, 426 (1911).

Since the clay used in making cement contains in some cases as high as 3 or 4 per cent of potash, it might be expected that part would escape from the kiln and be collected with the flue dust, particularly in those plants where the Cottrell process for collecting dust had been installed. This has been observed by several investigators to really take place, and the potash then collected is found to be in the soluble form. By the substitution of feldspar for clay in the manufacture of cement the potash then collected would, no doubt, be greatly increased, but since the analyses of cement show the presence of alkalis, it follows that with the style of kilns now in use all the potash in feldspar could not be made available in this way. That a larger proportion of the potassium would be volatilized by substituting for a part of the lime sufficient calcium chloride to be equivalent to the potassium is evident from the experiments already referred to, and experiments are now being undertaken on a large scale to compare the practicability of this procedure with the simple ignition of feldspar and lime alone.

According to the census report for 1910 the Portland cement manufactured in the United States during the year 1909 amounted to 65,000,000 barrels, or 13,000,000 tons, valued at approximately \$53,000,000. The maximum quantity of potash which it would be possible to obtain by the use of feldspar in the manufacture of this quantity of cement can be calculated if the potash content of the feldspar is known. This varies up to about 16 per cent, but if half of this, or 8 per cent, be taken as the average percentage of potash in commercial feldspar then 1 part of feldspar combined with 3 parts of calcium carbonate, equal to 1.68 parts of calcium oxide, would yield 0.08 part of potash and 2.6 parts of cement. Therefore 13,000,000 tons of cement would produce 400,000 tons of potash. Again, quoting potash at 66 cents a unit, this would have a value of \$26,400,000, which is three times the value of the potash salts used in this country during the year referred to, and about twice the value of the imports for 1911. Whether or not this would cover the cost of the feldspar, its transportation, and the expenses incident to the recovery of the potash can only be determined by experimentation on a large scale, but the probability that potash salts can thus be obtained in large quantities as a by-product makes this method of getting at the potash in feldspar quite promising.

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